(19) World Intellectual Property Organization International Bureau



. | TOTALE BOULDON IN BOUND BOURD HIM IN HOUSE HOUSE

(43) International Publication Date 25 September 2003 (25.09.2003)

PCT

(10) International Publication Number WO 03/078689 A1

(51) International Patent Classification⁷: C23C 30/00, 14/02, 28/04 (US). INSPEKTOR, Aharon; 5515 Raleigh Street, Pittsburgh, PA 15218 (US).

(21) International Application Number: PCT/US03/06953

(74) Agents: PRIZZI, John, J. et al.; KENNAMETAL INC., P.O. BOX 231, 1600 Technology Way, Latrobe, PA 15650-0231 (US).

(22) International Filing Date: 6 March 2003 (06.03.2003)

(81) Designated States (national): AU, BR, CA, CN, IL, IN, JP, KR, MX, PL.

(25) Filing Language:

English JP, KR, MX, PI

(26) Publication Language: English

(84) Designated States (regional): European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR).

(30) Priority Data:

Published:

10/097,487 14 March 2002 (14.03.2002) U

- with international search report

(71) Applicant: KENNAMETAL INC. [US/US]; P.O. BOX 231, 1600 TECHNOLOGY WAY, LATROBE, PA 15650-0231 (US).

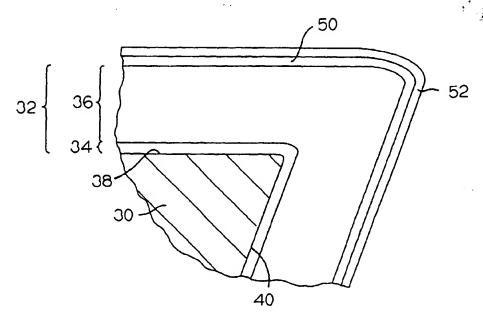
 before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

(72) Inventors: PENICH, Ronald, M.; 329 Center Avenue, GREENSBURG, PA 15601 (US). HEGDE, Parag, L.; 2006 Stone Cliffe Drive, MONROEVILLE, PA 15146

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

1, 14

(54) Title: NANOLAYERED COATED CUTTING TOOL AND METHOD FOR MAKING THE SAME



(57) Abstract: A nanolayered coated cutting tool (20) that includes a substrate (30) that has a surface (38, 40) with a coating (32) on the surface thereof. The coating comprises a plurality of coating sets of alternating nanolayers of metal aluminum nitride and metal nitride and/or metal aluminum carbonitride wherein each coating set has a thickness up to about 100 nanometers. The coating includes a bonding region (34) and an outer region (36). The bonding region (34) comprises a plurality of the coating sets wherein the thickness of each coating set increases as the set moves away from the surface of the substrate. The outer region (36) comprises a plurality of the coating sets wherein the thickness of each coating set is about equal.

NANOLAYERED COATED CUTTING TOOL AND METHOD FOR MAKING THE SAME

FIELD OF THE INVENTION

The invention pertains to a multi-layered

5 coated cutting tool and a method for making the same.

More particularly, the invention pertains to a

nanolayered coated cutting tool and a method for making
the same. In this regard, a nanolayered coated cutting
tool has a coating scheme that comprises adjacent

10 coating nanolayers having thicknesses of about 100
nanometers or less.

BACKGROUND OF THE INVENTION

Multi-layered coated cutting tools
demonstrate excellent metalcutting properties in

15 certain circumstances. Typically, a multi-layered
coated cutting tool comprises a substrate with a
plurality of coating layers deposited thereon. In some
cases the coating layers comprise a plurality of sets
of alternating coating layers. In this regard, U.S.

- Patent No. 6,103,357 to Selinder et al. for a
 MULTILAYERED COATED CUTTING TOOL shows a multi-layered
 non-repetitive coating scheme in which the layers have
 a thickness that ranges between 0.1 to 30 nanometers.
 PCT Patent Application W098/44163 to Sjöstrand et al.
- for a MULTILAYERED COATED CUTTING TOOL shows a multilayered repetitive coating scheme in which each repeat period has a thickness that ranges between 3 and 100 nanometers.

Other exemplary coating schemes comprise

30 multi-layered titanium nitride/titanium aluminum
nitride coatings deposited by physical vapor deposition
(PVD) techniques. Such coating schemes are described
in Hsieh et al., "Deposition and Characterization of

TiAlN and multi-layered TiN/TiAlN coatings using unbalanced magnetron sputtering", Surface and Coatings Technology 108-109 (1998) pages 132-137 and Andersen et al., "Deposition, microstructure and mechanical and 5 tribological properties of magnetron sputtered TiN/TiAlN multilayers", Surface and Coatings Technology 123 (2000) pages 219-226.

Even though multi-layered titanium nitride/titanium aluminum nitride coating schemes 10 exist, for a coating to be effective it must possess a certain minimum adhesion to the substrate and it must exhibit a certain minimum hardness. It has always been, and still remains, a goal to improve the adhesion of the coating to the substrate of the coated cutting 15 tool. In addition, it has always been, and still remains, a goal to optimize the hardness of the coated cutting tool. It has always been, and still remains, a goal to improve and optimize the combination of the properties of adhesion and hardness for a coated cutting tool.

It would thus be desirable to provide a coated cutting tool (e.g., a nanolayered coated cutting tool), as well as a method for making the coated cutting tool, wherein the cutting tool possesses improved adhesion and optimized hardness, as well as an improvement in the combination of the adhesion and hardness.

20

30

35

It would also be desirable to provide a metal nitride/metal aluminum nitride coated cutting tool (e.g., a nanolayered titanium nitride/titanium aluminum nitride coated cutting tool), as well as a method for making the coated cutting tool, wherein the cutting tool possesses improved adhesion and optimized hardness, as well as an improvement in the combination of the adhesion and hardness.

It would also be desirable to provide a metal aluminum nitride/metal aluminum carbonitride coated cutting tool (e.g., a nanolayered titanium aluminum nitride/titanium aluminum carbonitride coated cutting tool), as well as a method for making the coated cutting tool, wherein the cutting tool possesses improved adhesion and optimized hardness, as well as an improvement in the combination of the adhesion and hardness.

It would also be desirable to provide a metal nitride/metal aluminum nitride/metal aluminum carbonitride coated cutting tool (e.g., a nanolayered titanium nitride/titanium aluminum nitride/metal aluminum carbonitride coated cutting tool), as well as a method for making the coated cutting tool, wherein the cutting tool possesses improved adhesion and optimized hardness, as well as an improvement in the combination of the adhesion and hardness.

SUMMARY OF THE INVENTION

20 In one form, the invention is a nanolayered coated member that comprises a substrate that has a surface and a coating on the surface of the substrate. The coating comprises a plurality of coating sets of nanolayers wherein a set comprises alternating nanolayers of a nanolayer of a metal nitride (wherein 25 the metal nitride may optionally include carbon and/or silicon) and a nanolayer of a metal aluminum nitride (wherein the metal aluminum nitride may optionally include carbon and/or silicon). The coating includes a bonding region and an outer region. The bonding region 30 comprises a plurality of the coating sets wherein the thickness of a coating set generally increases as one moves away from the surface of the substrate. The outer region comprises a plurality of the coating sets.

WO 03/078689 PCT/US03/06953

-4-

The metal may comprise titanium, niobium, hafnium, vanadium, tantalum, zirconium and/or chromium alone or in combination with each other or in combination with other metals including aluminum in the metal nitride layer so long as the composition of the metal nitride layer differs from that of the metal aluminum nitride layer.

10

15

20

25

30

35

In another form, the invention is a nanolayered coated member that comprises a substrate that has a surface and a coating on the surface of the substrate. The coating comprises a plurality of coating sets of nanolayers wherein a set comprises alternating nanolayers of a nanolayer of a metal aluminum nitride (wherein the metal aluminum nitride may optionally include carbon and/or silicon) and a nanolayer of a metal aluminum carbonitride (wherein the metal aluminum carbonitride may optionally include silicon). The coating includes a bonding region and an outer region. The bonding region comprises a plurality of the coating sets wherein the thickness of a coating set generally increases as one moves away from the surface of the substrate. The outer region comprises a plurality of the coating sets. The metal may comprise titanium, niobium, hafnium, vanadium, tantalum, zirconium and/or chromium alone or in combination with each other or in combination with other metals.

In yet another form, the invention is a nanolayered coated member that comprises a substrate, that has a surface and a coating on the surface of the substrate. The coating comprises a plurality of coating sets of nanolayers wherein a set comprises alternating nanolayers of a nanolayer of a metal nitride (wherein the metal nitride may optionally include carbon and/or silicon), a nanolayer of a metal aluminum nitride (wherein the metal aluminum nitride

may optionally include carbon and/or silicon), and a nanolayer of a metal aluminum carbonitride (wherein the metal aluminum carbonitride may optionally include silicon). The coating includes a bonding region and an 5 outer region. The bonding region comprises a plurality of the coating sets wherein the thickness of a coating set generally increases as one moves away from the surface of the substrate. The outer region comprises a plurality of the coating sets. The metal may comprise titanium, niobium, hafnium, vanadium, tantalum, zirconium and/or chromium alone or in combination with each other or in combination with other metals including aluminum in the metal nitride layer so long as the composition of the metal nitride layer differs from that of the metal aluminum nitride layer and metal aluminum carbonitride layer.

In still another form thereof, the invention is a process for making a nanolayered coated member, the process comprising the steps of: providing a 1-2-3 substrate having a surface; providing a metal target 20 (wherein the metal target may optionally include carbon and/or silicon); providing a metal-aluminum target (wherein the metal-aluminum target may optionally include carbon and/or silicon); rotating a substrate between the metal target and the metal-aluminum target; 25 supplying electrical power at a first level of electrical power to the metal target; supplying electrical power at the first level to the metalaluminum target; depositing a coating comprising coating sets of alternating nanolayers on the surface 30 of the substrate; changing the deposition rate of the alternating nanolayers over a selected period of time during which electrical power supplied to the metal target changes from the first level to a second level; and controlling the deposition rate of the alternating 35

WO 03/078689 PCT/US03/06953

5

10

15

20

25

30

-6-

nanolayers for a period of time after the electrical power reaches the second level. The metal may comprise titanium, niobium, hafnium, vanadium, tantalum, zirconium and/or chromium alone or in combination with each other or in combination with other metals including aluminum in the metal target so long as the composition of the metal target differs from that of the metal-aluminum target.

In still another form thereof, the invention is a process for making a nanolayered coated member, the process comprising the steps of: providing a substrate having a surface; providing a metal-aluminum target (wherein the metal-aluminum target may optionally include carbon and/or silicon); providing a metal-aluminum-carbon target (wherein the metalaluminum-carbon target may optionally include silicon); rotating a substrate between the metal-aluminum target and the metal-aluminum-carbon target; supplying electrical power at a first level to the metal-aluminum target; supplying electrical power at the first level to the metal-aluminum-carbon target; depositing a coating comprising coating sets of alternating nanolayers on the surface of the substrate; changing the deposition rate of the alternating nanolayers over a selected period of time during which electrical power supplied to the metal-aluminum target and the metalaluminum-carbon target changes from the first level to a second level; and controlling the deposition rate of the alternating nanolayers for a period of time after the electrical power reaches the second level. metal may comprise titanium, niobium, hafnium, vanadium, tantalum, zirconium and/or chromium alone or in combination with each other or in combination with other metals.

In still another form thereof, the invention is a process for making a nanolayered coated member, the process comprising the steps of: providing a substrate having a surface; providing a metal target (wherein the metal target may optionally include carbon 5 and/or silicon); providing a metal-aluminum target (wherein the metal-aluminum target may optionally include carbon and/or silicon); providing a metalaluminum-carbon target (wherein the metal-aluminumcarbon target may optionally include silicon); rotating 10 a substrate between the metal target and the metalaluminum target and the metal-aluminum-carbon target; supplying electrical power at a first level to the metal target; supplying electrical power at the first level to the metal-aluminum target; supplying electrical power at the first level to the metalaluminum-carbon target; depositing a coating comprising coating sets of alternating nanolayers on the surface of the substrate; changing the deposition rate of the alternating nanolayers over a selected period of time 20 during which electrical power supplied to the metal target and to the metal-aluminum target and to the metal-aluminum-carbon target changes from the first level to a second level; and controlling the deposition 25 rate of the alternating nanolayers for a period of time after the electrical power reaches the second level. The metal may comprise titanium, niobium, hafnium, vanadium, tantalum, zirconium and/or chromium alone or in combination with each other or in combination with other metals including aluminum in the metal target so 30 long as the composition of the metal target differs from that of the metal-aluminum target and the metalaluminum-carbon target.

10

15

20

25

...

BRIEF DESCRIPTION OF THE DRAWINGS

The following is a brief description of the drawings that form a part of this patent application:

FIG. 1 is an isometric view of a specific embodiment of a nanolayered coated cutting tool;

FIG. 2 is schematic cross-sectional view of a cutting edge of the nanolayered coated cutting tool of FIG. 1 showing the substrate with the nanolayered coating comprising a bonding region and an outer region, and also including a finishing layer and a lubricious layer;

FIG. 3 is a photomicrograph taken via transmission electron microscopy (TEM) technique of the interface between the coating and the substrate for the nanolayered coated cutting tool of Example 276;

FIG. 4 is a photomicrograph taken via transmission electron microscopy (TEM) technique of the mid-section of the coating for the nanolayered coated cutting tool of Example 276; and

FIG. 5 is a photomicrograph taken via transmission electron microscopy (TEM) technique of the surface region of the coating for the nanolayered coated cutting tool of Example 276.

DETAILED DESCRIPTION

Referring to the drawings, FIG. 1 illustrates a specific embodiment of a cutting tool generally designated as 20. Cutting tool 20 has a top rake surface 22 and flank surfaces 24. The top rake surface 22 intersects with the flank surfaces 24 so as to form cutting edges 26 at the intersections thereof. 30

As shown in FIG. 2, cutting tool 20 comprises a substrate 30 that has a nanolayered coating as shown by brackets 32. The nanolayered coating 32 comprises a bonding region as shown by the brackets 34 in FIG. 2.

The bonding region 34 comprises one or more coating sets of nanolayers (and typically a plurality of coating sets of nanolayers) as described hereinafter. The nanolayered coating 32 also includes an outer region as shown by brackets 36 in FIG. 2. The outer region comprises a plurality of coating sets of nanolayers as described hereinafter.

FIG. 2 shows that the nanolayered coating 32 has been applied to the rake surface 38 and the flank surface(s) 40 of the substrate 30. However, it should be appreciated that there are instances in which the nanolayered coating 32 may only be applied to a selected one of the surfaces or selected portions of the surfaces of the substrate.

We among the control of the grant of the control of manufacture of the nanolayered coating, the nanolayered coating may comprise two or more coating sets of alternating layers The rate of the materials wherein one of the materials is a metal of the materials as a metal of the second of the materials as a metal of the second of the materials as a metal of the second of the nitride and the other material is a metal aluminum 20 nitride (e.g., titanium nitride/titanium aluminum nitride or titanium aluminum nitride/titanium nitride). What this means is that in one specific coating scheme, the metal nitride (e.g., titanium nitride) layer may be the layer closest to (or actually on) the surface of the substrate. Yet, in another specific coating scheme, the metal aluminum nitride (titanium aluminum nitride) layer may be the layer closest to (or actually on) the surface of the substrate. Applicants contemplate that metal nitrides and metal aluminum nitrides of the following metals and their alloys would 30 be acceptable for use in the nanolayered coating: titanium, niobium, hafnium, vanadium, tantalum, zirconium, and/or chromium alone or in combination with each other or in combination with other metals. metal nitride layer may include aluminum so long as the 35

WO 03/078689 PCT/US03/06953

5

10

15

20

25

30

- 1

-10-

composition of the metal nitride layer differs from that of the metal aluminum nitride layer. The metal nitride and the metal aluminum nitride each may include (as an optional component) carbon and/or silicon.

Still making general reference to another arrangement of the nanolayered coating, the nanolayered coating may comprise two or more coating sets of alternating layers of materials wherein one of the materials is a metal aluminum nitride and the other material is a metal aluminum carbonitride (e.g., titanium aluminum nitride/titanium aluminum carbonitride or titanium aluminum carbonitride/titanium aluminum nitride). What this means is that in one specific coating scheme, the metal aluminum nitride (e.g., titanium aluminum nitride) layer may be the layer closest to (or actually on) the surface of the substrate. Yet, in another specific coating scheme, the metal aluminum carbonitride (e.g., titanium aluminum carbonitride) layer may be the layer closest to (or actually on) the surface of the substrate. Along the lines of the metal nitride/metal aluminum nitride coating sets, applicants contemplate that the following metals and their alloys would be acceptable for use with the nanolayered coating: titanium, niobium, hafnium, vanadium, tantalum, zirconium, and/or chromium alone or in combination with each other or in combination with other metals. The metal aluminum nitride may include (as optional components) carbon and/or silicon. The metal aluminum carbonitride may include (as an optional component) silicon.

Might President

Referring to still another arrangement of the nanolayered coating, the nanolayered coating may comprise alternating layers of a metal nitride, a metal aluminum nitride and a metal aluminum carbonitride.

35 Various arrangements of these nanolayers are presented

as follows when the metal is titanium: titanium nitride/titanium aluminum nitride/titanium aluminum carbonitride or titanium aluminum carbonitride/titanium aluminum nitride/titanium nitride or titanium aluminum carbonitride/titanium nitride/titanium aluminum nitride or titanium aluminum nitride or titanium aluminum carbonitride/titanium nitride or titanium nitride/titanium aluminum carbonitride/titanium aluminum carbonitride/titanium nitride/titanium nitride/titanium aluminum nitride/titanium nitride/titanium aluminum carbonitride/titanium nitride/titanium aluminum carbonitride.

In one group of these arrangements with titanium as the metal, the titanium nitride layer may be the layer closest to (or actually on) the surface of the substrate. In this group, the titanium aluminum nitride layer and the titanium aluminum carbonitride layer are the other layers.

In another group of these arrangements, the titanium aluminum nitride layer may be the layer closest to (or actually on) the surface of the substrate. In this group, the titanium nitride layer and the titanium aluminum carbonitride layer are the other layers.

In still another group of the arrangements, the titanium aluminum carbonitride layer may be the layer closest to (or actually on) the surface of the substrate. In this group, the titanium nitride layer and the titanium aluminum nitride layer are the other layers.

Although the specific compounds for the

coating arrangements set forth above are titanium
nitride, titanium aluminum nitride and titanium
aluminum carbonitride, applicants contemplate that
other metal nitrides, metal aluminum nitrides and metal
aluminum carbonitrides would be acceptable. In this
regard, other metals and their alloys for the metal

20

25

30

35

47 - 11

.

nitride, the metal aluminum nitride, and the metal aluminum carbonitride include niobium, hafnium, vanadium, tantalum, zirconium, and/or chromium alone or in combination with each other or in combination with other metals. The metal nitride layer may include aluminum so long as the composition of the metal nitride layer differs from the composition of the metal aluminum nitride layer and the metal aluminum carbonitride layer. In the above arrangements, the metal nitride (e.g., titanium nitride) and the metal aluminum nitride (e.g. titanium aluminum nitride) each may (as an option) include carbon and/or silicon. metal aluminum carbonitride (e.g., titanium aluminum carbonitride) may as an optimal component include 15 silicon.

Referring back to the specific coating scheme shown in FIG. 2, the bonding region 34 comprises a plurality of coating sets of alternating nanolayers of titanium nitride and titanium aluminum nitride. The purpose of the bonding region is to provide good adhesion between the coating and the substrate during usage (e.g., metalcutting applications). The bonding region has a thickness that ranges between about .025 micrometers and about 0.6 micrometers. More preferably, the bonding region has a thickness than ranges between about 0.05 micrometers and about 0.4 micrometers. Each nanolayer in the bonding region (whether it is a nanolayer of titanium nitride or a nanolayer of titanium aluminum nitride) has a thickness that may range between about 0.5 nanometers and about 5 nanometers, and more preferably, may range between about 0.5 nanometers and about 2 nanometers.

The thickness of the titanium aluminum nitride layer is typically different than the thickness of the titanium nitride layer. Generally speaking, the

thickness of a coating layer varies due to one or more factors where in these factors are set out below without limitation.

The coating sets that comprise the bonding region are deposited during the so-called "ramp up" 5 portion of the coating process. The "ramp up" portion of the process occurs during the initial part of the process in which the deposition rate is increased from a first level to a second level. Although it depends upon the time to complete the so-called "ramp up" 10 portion of the process, the number of coating sets of layers may extend into the hundreds since each coating set has a thickness in the nanometer range (i.e., a thickness of less than about 100 nanometers).

As a result of this continuing increase in the deposition rate during the ramp up period, the thickness of the coating sets in the bonding region changes. More specifically, it is generally the case that as one moves away from the surface of the substrate, the thickness of each coating set increases (typically gradually) until the thickness of each coating set reaches a point at which the coating sets exhibit a generally consistent thickness. In the process, the deposition rate increases during the ramp up period, which results in the increase in thickness. 25 The increase in deposition may be due to (without limitation) any one or more of the following factors: the gas composition in the chamber, the gas flow rate in the chamber, the sputtering rate of the target and/or the level of electrical power supplied to the 30 target.

It should be appreciated that the increase in the thickness of each coating set may be due to each of the nanolayers increasing in thickness. As an alternative, the increase in the thickness of each

35

WO 03/078689 PCT/US03/06953

-14-

coating set may occur when the thickness of one nanolayer remains substantially constant and the thickness of the other nanolayer increases.

5

10

15

20

25

30

35

In the process, for example, once the electrical power to the targets reaches the second level of electrical power, the electrical power preferably will be reduced for at least one of the targets to a level greater than the first level of electrical power for the remainder of the coating process to apply the outer region. The reduced level of electrical power may be different for each target. Also, the level of electrical power applied to each target may vary during the portion of the process to apply the outer region.

Referring to the bonding region, for example, the titanium nitride layer and the titanium The state of the state of the carbonitride layer may include an aluminum content 5 4 7 4 7 6 33 7 4 43 ranging from 0 to a higher level so long as the amount of the agency with of aluminum is less than that contained in the titanium aluminum nitride layers and in the titanium aluminum carbonitride layers.

> Still referring to FIG. 2, the plurality of coating sets that comprise the outer region are alternating nanolayers of titanium nitride and titanium aluminum nitride. The outer region has a thickness that ranges between about 1 micrometer and about 20 micrometers so long as there is good adhesion between the coating and the substrate in metalworking applications. More preferably, the outer region has a thickness that ranges between about 1 micrometer and about 10 micrometers. Each nanolayer (whether it is titanium nitride or titanium aluminum nitride) has a thickness that may range between about 0.5 nanometers and about 20 nanometers. More preferably, the thickness of each such nanolayer ranges between about

0.5 nanometers and about 10 nanometers. Most preferably, the thickness of each such nanolayer ranges between about 0.5 nanometers and about 2 nanometers.

The thickness of each coating set in the outer region may be substantially equal or the thicknesses may vary. In the situations in which the coating sets have a substantially equal thickness, the thickness of the nanolayers that make up the coating set, i.e., titanium nitride nanolayer and the titanium aluminum nitride nanolayer, may not necessarily be 10 equal. In fact, as will be seen from the description hereinafter of the coating scheme in FIG. 3, the thickness of the titanium nitride nanolayer ranges between about 1 nanometer to about 2 nanometers and the 15 thickness of the titanium aluminum nitride nanolayer ranges between about 10 nanometers to about 11 nanometers. In this regard, the thickness of the titanium nitride nanolayers in the bonding region also Company of the Section of the Section range between about 1 nanometer to about 2 nanometers

- while the thickness of the titanium aluminum nitride nanolayers increase as the coating sets move away from the substrate. Applicants contemplate that the titanium nitride nanolayer can preferably range in thickness between about 0.5 to about 2 nanometers.
- Applicants also contemplate that the titanium aluminum nitride nanolayer can preferably range in thickness between about 0.5 to about 11 nanometers.

As mentioned above, because the sputtering rate for the titanium-aluminum target is greater than the sputtering rate for the titanium target, generally speaking, the thickness of each nanolayer of titanium aluminum nitride may be greater than the thickness of each nanolayer of titanium nitride.

Referring to FIG. 2, layer 50 is a finishing 35 layer that may comprise titanium nitride or titanium

aluminum nitride. The thickness of finishing layer 50 is between about 0.1 micrometers and about 3 micrometer. Applicants contemplate that metal nitrides, metal aluminum nitrides and metal aluminum carbonitrides would be acceptable as the finishing layer. In this regard, other metals and their alloys for the metal nitride, the metal aluminum nitride, and the metal aluminum carbonitride include titanium, niobium, hafnium, vanadium, tantalum, zirconium, and/or chromium alone or in combination with each other or in combination with other metals. The finishing layer alternately or in addition to the above finishing layers may be an alumina layer. The finishing layer is typically applied by physical vapor deposition (PVD) techniques. Layer 52 is a lubricious layer that may comprise a material like molybdenum disulfide. total thickness of finishing layer 50 and lubricious layer 52 is between about 0.1 micrometer and about 3 micrometers. The finishing layer and the lubricious layer are each optional layers for the coating scheme.

公主 人名英马克

2000

esista di

10

15

20

25

30

35

Still referring to FIG. 2, the substrate 30 is typically a hard material such as cemented carbide. One exemplary composition for the substrate 30, which is substrate A, is a cemented (cobalt) tungsten carbide material that has up to 0.1 weight percent tantalum, up to 0.1 weight percent niobium, up to 0.1 weight percent titanium, between about 0.3 and about 0.5 weight percent chromium, between about 5.7 weight percent and 6.3 weight percent cobalt with the balance being tungsten and carbon wherein most of the tungsten and carbide is in the form of tungsten carbide. The substrate has a hardness between about 92.6 and about 93.4 Rockwell A, a coercive force (H_C) of between about 250 and about 320 oersteds, a specific gravity of between about 14.80 and about 15.00 grams per cubic

centimeter, a tungsten carbide grain size of 1-5 micrometers, and a magnetic saturation of between 167.7 and 191.9 microTesla cubic meter per kilogram cobalt. As will be discussed hereinafter, the coated cutting inserts used in the turning tests comprised a substrate of the same composition as substrate A.

Another exemplary composition for the substrate, which is substrate B, is a cemented (cobalt) tungsten carbide material that has between about 1.2 to about 2.5 weight percent tantalum, between about 0.3 to 10 about 0.6 weight percent niobium, up to 0.4 weight percent titanium, between about 11 weight percent and 12 weight percent cobalt with the balance being tungsten and carbon wherein most of the tungsten and 15 carbide is in the form of tungsten carbide. The substrate has a nominal hardness of about 89.8 Rockwell た。Me 1.750年には、1975年に対象。as.coercivesforces(H_c)、ofobetween、about 145 and about 1.751年の 27 年 Figure 1985 December 185 coersteds, apspecific gravity of between about 14.1 and about 14.5 grams per cubic centimeter, a tungsten of the continue of the c carbide grain size of 1-6 micrometers, and a magnetic saturation of between 167.7 and 187.9 microTesla cubic meter per kilogram cobalt. As will be discussed hereinafter, the coated cutting inserts used in the milling tests comprised a substrate of the same composition as Substrate B. 25

The substrate may also be a cermet, a ceramic or a high speed steel, polycrystalline cubic boron nitride, polycrystalline diamond or diamond sheet or diamond film. The substrate may take the form of an indexable cutting insert, a cutting insert, a drill, milling cutter, end mill, reamer or tap made of any of the foregoing substrate materials.

The preferred adhesion strength of the coating to the surface of the substrate is at least 45 kilograms (kg). More preferably, the adhesion strength

10

20

25

30

is at least 60 kg, and most preferably the adhesion strength is at least 100 kg. The test to determine the adhesion strength is a Rockwell A indentation test.

The preferable thickness of the entire nanolayered coating, exclusive of a finishing layer and a lubricious layer, is between about 1 micrometers and about 21 micrometers, and more preferably the thickness is between about 1 micrometers and about 11 micrometers, and most preferably the thickness of the entire nanolayered coating is between about 2 micrometers and about 6 micrometers.

Generally speaking, the process to produce the coatings comprises using a physical vapor deposition technique such as magnetron sputtering. 15 the following examples, the apparatus used to apply the coating was a Cemecon CC800/8 magnetron sputtering coating reactor. The coating reactor was configured so that the cutting insert substrates were rotated between two sets of targets. Each set of targets was disposed 180° from the other set. One of the sets of targets was two targets of titanium and the other set of targets was two titanium-aluminum targets. The substrate table was rotated at a rate of 0.8 revolutions per minute. The substrates were mounted on rotating planetary rod fixtures on the substrate table.

In these examples, the process comprises two basic portions. The first is the so-called "ramp up" portion which the power to the targets is increased from about 500 watts to a target power, such as, for example, about 8000 watts, over the course of about 45 minutes. Once the power reached its target, then as one alternative it is adjusted so as to remain constant (which may be, for example, 8000 watts or a lower electrical power level) throughout the balance of the coating process. As another option, the electrical

power may be varied during the balance of the coating process. The nature of the variation may be, for example, as a sinusoidal wave or as a square tooth wave or as a saw tooth wave.

5 The following examples were made in a fashion generally consistent with the above description of the coating process. Each of the examples in Table I includes substrates that had a composition like that of Substrate A and substrates that had a composition like that of Substrate B. The titanium target was solid 10 titanium metal. The titanium-aluminum target comprised a titanium metal target having forty-eight plugs of aluminum therein. The process parameters for each one of these examples are set forth in Table I below.

Table I 15 Process Parameters for Examples of Titanium Nitride/Titanium Aluminum Nitride Nanolayer Coatings

					vanjenaje		•
Example	Ti Target Power (KW)	TiAl Target Power (KW)	Argon Flow Rate (sccm)	Nitrogen Flow Rate (sccm)	Coating Time (hours)	Bias Current (Amps)	Nitrogen Partial Flow Rate
274	4	6	175	~113	6	21	0.31
276	4	8	175	~120	6	26	0.32
277	8	4	175	~119	6	25	0.32
281	4	6	175/100	~180	6	20	0.5
418	1.6	8	210	~ 90	6	21	.24
422	1.6	8	210	~ 88	6	20	.24

In each one of these examples, the flow rate for the Krypton was 80 standard cubic centimeter per minute 20 (sccm). In Table I the designation "sccm" for the argon and nitrogen flow rate is standard cubic

Service Advanced to

· 15

20

25

30

centimeter per minute. In Table I the nitrogen partial flow rate equals the flow rate of nitrogen (sccm) divided by the sum of the flow rates of nitrogen, argon and Krypton (sccm). For Example 281 in Table I, the argon flow rate of 175 sccm existed at the start of the ramp up period and decreased during the ramp up period to a flow rate equal to 100 sccm which was maintained during the remainder of the coating process.

In the processing, there is control over the aluminum content of the titanium aluminum nitride depending upon the specific metalcutting application. For some applications it is generally preferred that the aluminum/titanium atomic ratio (Al/Ti atomic ratio) is less than 1.0. In these applications, a preferred range for the Al/Ti atomic ratio is between about 0.2 and about 0.9. For other applications it is generally preferred that the Al/Ti atomic ratio be greater than or equal to 1.0 wherein a preferred range for the Al/Ti atomic ratio is between 1.0 and about 2.5. The limitation of the higher end range is based upon the ability of the coated cutting insert to have adequate hardness for metalcutting applications.

To increase the Al/Ti atomic ratio one may increase the level of electrical power to the aluminumcontaining target(s) and/or control the nitrogen partial flow rate. To obtain a maximum aluminum content with a constant electrical power to the aluminum-containing target(s), one can decrease the nitrogen partial flow rate. One preferred nitrogen partial flow rate is a rate below 0.5. A more preferred nitrogen partial flow rate is a rate below 0.4. A still more preferred nitrogen partial flow rate is a rate less than 0.35. If the nitrogen partial flow rate is below 0.2, then the adhesion and hardness of

the layers decreases. Overall, the preferred range for the nitrogen partial flow rate is between 0.2 and 0.35.

Table II below sets forth the process parameters for Example 449. The ramp up for Example 449 was the same as for the earlier examples, except 5 that the titanium targets were replaced by titaniumaluminum-carbon targets. Each titanium-aluminum-carbon target comprised twelve plugs of aluminum and twelve plugs of graphite in a titanium metal target.

Table II - Process Parameters for Example 449 (Titanium Aluminum Carbonitride/Titanium Aluminum Nitride Nanolayer Coatings)

্ কেন্দিল ই হিন্তু কুটা ই ১১১		TiAIC Target Power (KW)	TiAI Target Power (KW)	Argon Flow Rate (sccm)	Nitrogen Flow Rate (sccm)	Coating Time (hours)	Bias Current (Amps)	Nitrogen Partial Flow Rate		
			1.6	210	87	6	15	0.23	e,	
	For the	proces	sing o	f Examp		#ho 61-		· · · · · · · · · · · · · · · · · · ·	er en	

For the processing of Example 449, the flow of Krypton gas remained constant at a rate of 80 standard cubic centimeter per minute. In Table II the designation "sccm" for the argon and nitrogen flow rate is standard cubic centimeter per minute.

Table III below sets forth the process parameters for Example 394. The ramp up for Example 394 was the same as that for Example 449, except that 20 the titanium-aluminum targets were replaced by titanium targets. Each titanium-aluminum-carbon target comprised twelve plugs of aluminum and twelve plugs of graphite in a titanium metal target.

10

20

25

Table III - Process Parameters for Example 394 (Titanium Aluminum Carbonitride / Titanium Nitride Nanolayer Coatings)

Example	TiAIC Target Power (KW)	Ti Target Power (KW)	Argon Flow Rate (sccm)	Nitrogen Flow Rate (sccm)	Coating Time (hours)	Bias Current (Amps)	Nitrogen Partial Flow Rate
394	8	1.6	210	80	6	20	0.22

For the processing of Example 394, the flow of Krypton gas remained constant at a rate of 80 milliliters per In Table III the designation "sccm" for the argon and nitrogen flow rate is standard cubic centimeter per minute.

Selected properties of the resultant coated 10 cutting tool are set forth in Table IV below. These properties are the aluminum/titanium atomic ratio, the overall thickness of the coating in micrometers, the microhardness of the cutting tool in kilograms per square millimeter (kg/mm²) as measured by a standard Vickers test at a 25 gram load and the indent adhesion strength of the coated cutting tool as measured in kilograms.

Referring to the analysis of the coating layers, a JEOL 6400 Scanning Electron Microscope (SEM) with an Oxford Industries INCA Energy 400 Dispersive X-Ray Spectroscopy (EDS) is used to collect compositional information about the coatings (i.e., the titanium aluminum nitride coatings). Oxford Industries is located at 130A Baker Avenue Ex, Concord, MA 01742 and JEOL USA, Inc. is located at 11 Dearborn, Peabody, MA 01960.

The coating is analyzed in the as deposited state with no additional sample preparation or

conductive coating applied. X-Rays are collected using a 15KV accelerating voltage.

The coating must be a minimum of about 3 micrometers in thickness to prevent the excitation of the substrate by the electron beam (thicker coatings 5 would be necessary if a higher accelerating voltage was used). A minimum of 5 spectra are collected and the results quantified. The apparent concentration of each element is equal to the intensity of that element in the sample times the weight percent of that element in the standard divided by the intensity of the element in the standard. This must then be corrected for interelement effects so that the weight percent of the element is equal to the apparent concentration divided by the intensity correction. Atomic percentages are a first and the then calculated by dividing the weight percent by the control of t atomic weight of the element. There are several to be a first and the several to be a first as a several to be a first as methods of calculating intensity corrections. This particular analytical scheme uses a Phi-Rho-Z approach. Since correction factors are dependent on the composition of the sample, true concentrations are derived using an iterative calculation.

10

15

20

Table IV						
Selected Properties of the Examples Using Substrate A						

Example	Al/Ti Atomic Ratio (%)	Thickness (μm)	Average Values of Vickers Microhardness (kg/mm²)	Indent Adhesion Strength (kg)
274	0.6	3.4/4.1/3.4	2770 ± 101	> 60
276	0.67	3.9/4.1/3.8	3051 ± 133	> 60
277	0.25	4.1/3.9/3.6	2856 ± 071	> 60
281	0.46	3.2/2.8/2.9	2767 ± 169	> 60
418	1.1	4.5/5.6/5.3	2774 ± 32	> 60
422	1.18	3.6/3.6/4.0	2818 ± 245	> 60
394	0.24 [4.9 atomic % carbon present]	4.2/4.1/4.0	3016 ± 133	> 60
449	0.36 [2.9 atomic % carbon present]	4.4/4.2/3.9	2899 ± 60	> 60

The examples set out in Table IV used substrates that had a composition like that of Substrate A. For the properties listed in Table IV, applicants expect that the coated cutting inserts using a substrate that had a composition like Substrate B would exhibit the same or substantially similar properties.

Some of the examples were tested in a turning application. The turning parameters were: workpiece material was 304 stainless steel, the speed was 500 surface feet per minute (sfm) [152 meters per minute], the feed was 0.012 inches per revolution (ipr) [0.3 millimeters per revolution], the depth of cut was 0.080 inches (d.o.c.) [2 millimeters d.o.c.], and flood coolant. The cutting tool was a CNGP432 style of cutting tool with a negative 5 degrees lead angle and a sharp cutting edge. The results of the turning tests are set forth in Table III below.

1 - 1 - 7 - - -

and the street

The criteria for the tool life are as follows: uniform flank wear: 0.012 inches (0.3 millimeters); maximum flank wear: 0.016 inches (0.4 millimeters); nose wear: 0.016 inches

(0.4 millimeters); crater wear: 0.004 inches

(0.100 millimeters); chip width on rake: 0.020 inches

(0.5 millimeters); and depth of cut notch: 0.016 inches

(0.4 millimeters).

Table V Tool Life (Minutes) for Turning of 304 Stainless Steel

		Example	Rep. 1	Rep. 2	Average	Std. Deviation	
		277	18.00	14.30	16.15	2.62	
	,	274	14.93	23.56	19.24	6.11	
· · · ·		281	12.46	11.00	11.73	1.03	
1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	i i i i i i i i i i i i i i i i i i i		27.28	21.66 % (% A.S.)	24.57	3.97	
·,	i Maraja	KC5010 [Comparative Example]	14.00	16.00	15.00	1.41	

For Comparative Example KC5010, the substrate had the same composition as Substrate A. The coating was a single layer of titanium aluminum nitride with a nominal thickness of about 4.0 micrometers. Still 15 referring to Comparative Example KC5010, the Al/Ti ratio equaled about 1.0, and the microhardness equaled about 2500 Kg/mm^2 . The KC5010 cutting tool is a prior art cutting tool available from Kennametal Inc. of 20 Latrobe, Pennsylvania.

Referring to the photomicrograph FIG. 3, there is shown the bonding region and the outer region of the coating scheme from Example 276. For each one of the bonding region and the outer region there are

WO 03/078689 PCT/US03/06953

5

10

20

25

30

35

alternating nanolayers of titanium nitride and titanium aluminum nitride. The dark nanolayers are titanium nitride and the light nanolayers are titanium aluminum nitride.

For FIG. 3, and also FIGS. 4 and 5, it should be appreciated that applicants believe that the visual contrast in darkness between the nanolayers shows that the titanium nitride nanolayers have no aluminum contained therein, or significantly less aluminum contained therein than do the titanium aluminum nitride nanolayers. It should be appreciated that the titanium nitride nanolayers are not necessarily pure titanium nitride since they may contain aluminum. To the extent there is aluminum contained in the titanium nitride nanolayers, this aluminum content may vary between the titanium nitride nanolayers. Applicants believe that the splotchy areas in the figures, and especially FIG. 3, are artifacts of TEM specimen preparation.

Referring to the bonding region, the nanolayers of titanium nitride have a thickness of between about 1 to 2 nanometers. The thickness of the titanium nitride nanolayers remains substantially constant throughout the bonding region. The thickness of the titanium aluminum nitride nanolayers begins at a range between about 1 to about 2 nanometers at and near the interface between the coating and the substrate. The substrate is the black area in the upper right-hand corner of the photomicrograph. The thickness of the titanium aluminum nitride layers increases as one moves away from the surface of the substrate. The thickness of the titanium aluminum nitride nanolayers increases to a range between about 10 to about 11 nanometers.

Referring to the photomicrograph FIG. 4, there is shown the bulk region of the coating scheme. The bulk region comprises alternating nanolayers of

WO 03/078689

titanium nitride and titanium aluminum nitride wherein one nanolayer of titanium nitride and one nanolayer of titanium aluminum nitride comprises a coating set. The thickness of each nanolayer of titanium nitride is about equal and ranges between about 1 to about 2 nanometers. The thickness of each nanolayer of titanium aluminum nitride is about equal and ranges between about 10 nanometers to about 11 nanometers.

Referring to the photomicrograph FIG. 5,

there is shown the region of the coating scheme that includes the outer surface thereof. This region of the coating scheme comprises alternating nanolayers of titanium nitride and titanium aluminum nitride wherein one nanolayer of titanium nitride and one nanolayer of titanium aluminum nitride comprises a coating set. The thickness of each nanolayer of titanium nitride is about equal and ranges between about 1 to about 2 nanometers. The thickness of each nanolayer of titanium aluminum nitride is about equal and ranges between 20 about 10 nanometers to about 11 nanometers.

The examples were tested in a milling application. The milling parameters were: workpiece material was 4140 steel, the speed was 600 surface feet per minute (sfm) [183 meters per minute], the feed was 0.012 inches per revolution (ipr) [0.3 millimeters per revolution], the axial depth of cut (a.d.o.c.) was 0.100 inches [2.5 millimeters rdoc] and the radial depth of cut (r.d.o.c.) was 3.0 inches [75 millimeters rdoc], and flood coolant. The cutting tool was a SEHW43A6T style of cutting tool with a 45 degree lead angle and a T land of 0.2 millimeters and 20 degrees. The results of the milling tests are set forth in Table VI below.

The criteria for the tool life are as follows: uniform flank wear: 0.012 inches

£

15

20

- (0.3 millimeters); maximum flank wear: 0.016 inches
- (0.4 millimeters); nose wear: 0.016 inches
- (0.4 millimeters); crater wear: 0.004 inches
- (0.100 millimeters); and chip width on rake:
- 5 0.030 inches (0.75 millimeters). The examples set out in Table VI used a substrate that had a composition like Substrate B. Comparative Example KC525M is a cutting tool that has a substrate with a composition like that of Substrate B and a coating of titanium aluminum nitride wherein the coating has a nominal thickness of about 4 micrometers.

Table VI
Tool Life (Minutes) for Milling of 4140 Steel

Example	Rep. 1	Rep. 2	Rep. 3	Average Tool Life / Std. Deviation
277	7.45	6.62	9.10	7.72/1.26
274	7.45	8.28	8.28	8.00/0.48
281	4.96	7.45	8.28	6.90/1.73
276	8.28	4.97	8.28	7.18/1.91
KC525M [Comparative Example]	4.97	4.97	6.62	5.52/0.96

The patents and other documents identified herein are hereby incorporated by reference herein.

Other embodiments of the invention will be apparent to those skilled in the art from a consideration of the specification or a practice of the invention disclosed herein. It is intended that the specification and examples are illustrative only and are not intended to be limiting on the scope of the invention. The true scope and spirit of the invention is indicated by the following claims.

WHAT IS CLAIMED IS:

A nanolayered coated member comprising:
 a substrate having a surface and a coating on
the surface of the substrate;

the coating comprising a plurality of coating sets of nanolayers wherein each coating set comprising alternating nanolayers of a metal nitride and a metal aluminum nitride;

the coating including a bonding region and an outer region; and $\ \ _{\rm J}$

the bonding region comprising a plurality of the coating sets wherein the thickness of the coating sets increase as one moves away from the surface of the substrate.

- 2. The coated member according to claim 1 wherein the metal is selected from the group comprising titanium, niobium, hafnium, vanadium, tantalum, molybdenum, zirconium, chromium and tungsten alone or in combination with each other or in combination with other metals.
- 3. The coated member according to claim 1 wherein the substrate is selected from the group comprising cemented carbide, cermet, ceramic, high speed steel, diamond, polycrystalline diamond, and polycrystalline cubic boron nitride.
- 4. The coated member according to claim 1 wherein the coating has a thickness ranging between about 1 micrometer and about 21 micrometers.
- 5. The coated member according to claim 1 wherein the bonding region has a thickness ranging

between about 0.025 micrometers and about 0.6 micrometers.

- 6. The coated member according to claim 1 wherein the bonding region has a thickness ranging between about 0.05 micrometers and about 0.4 micrometers.
- 7. The coated member according to claim 1 wherein each one of the metal nitride nanolayers and each one of the metal aluminum nitride nanolayers in the bonding region has a thickness between about 0.5 nanometers and about 5 nanometers.
- 8. The coated member according to claim 1 wherein each one of the metal nitride nanolayers and each one of the metal aluminum nitride nanolayers in the bonding region has a thickness between about 0.5 nanometers and about 2 nanometers.
 - 9. The coated member according to claim 1 wherein the outer region has a thickness ranging between about 1 micrometer and about 20 micrometers.
 - 10. The coated member according to claim 1 wherein each one of the metal nitride nanolayers and each one of the metal aluminum nitride nanolayers in the outer region has a thickness between about 0.5 nanometers and about 20 nanometers.
 - 11. The coated member according to claim 1 wherein each one of the metal nitride nanolayers and each one of the metal aluminum nitride nanolayers in the outer region has a thickness between about 0.5 nanometers and about 10 nanometers.

* Y 6

- 12. The coated member according to claim 1 wherein each one of the metal nitride nanolayers and each one of the metal aluminum nitride nanolayers in the bonding region has a thickness between about 0.5 nanometers and about 2 nanometers.
- 13. The coated member according to claim 1 wherein the metal is titanium, and for each of the coating sets the titanium aluminum nitride nanolayer having a thickness and the titanium nitride nanolayer having a thickness, and the thickness of the titanium aluminum nitride nanolayer being different from the thickness of the titanium nitride nanolayer.
- 14. The coated member according to claim 1 wherein the metal is titanium, and for each of the coating sets the titanium aluminum nitride nanolayer having a thickness and the titanium nitride nanolayer having a thickness, and the thickness of the titanium aluminum nitride nanolayer being greater than the thickness of the titanium nitride nanolayer.
- 15. The coated member according to claim 14 wherein the thickness of the titanium nitride nanolayer remains substantially the same as one moves away from the surface of the substrate.
- 16. The coated member according to claim 13 wherein each nanolayer of the titanium nitride in the bonding region has a thickness ranging between about 0.5 nanometers and about 2 nanometers.
- 17. The coated member according to claim 13 wherein each nanolayer of the titanium aluminum nitride in the bonding region has a thickness ranging between about 0.5 nanometers and about 11 nanometers.

- 18. The coated member according to claim 13 wherein each nanolayer of titanium nitride in the outer region has a thickness ranging between about 0.5 nanometers and about 2 nanometers.
- 19. The coated member according to claim 13 wherein each nanolayer of titanium aluminum nitride in the outer region has a thickness ranging between about 0.5 nanometers and about 11 nanometers.
- 20. The coated member according to claim 1 wherein for each of the coating sets in the bonding region the thickness of the metal nitride nanolayer being different from the thickness of the metal aluminum nitride nanolayer.
- wherein for each of the coating sets in the bonding region, the metal aluminum nitride nanolayer having a greater thickness than the thickness of the metal nitride nanolayer.
 - 22. The coated member according to claim 1 wherein for each of the coating sets in the outer region the thickness of the metal nitride nanolayer being different from the thickness of the metal aluminum nitride nanolyer.
 - 23. The coated member according to claim 22 wherein for each of the coating sets in the outer region, the metal aluminum nitride nanolayer having a greater thickness than the thickness of the metal nitride nanolayer.
 - 24. The coated member according to claim 22 wherein for each of the coating sets in the outer region the thickness of the metal aluminum nitride

nanolayer being at least about five times as great as the thickness of the metal nitride nanolayer.

- 25. The coated member according to claim 1 wherein the coated member comprising one of the following: a cutting insert, an indexable cutting insert, a drill, a milling cutter, an end mill, a reamer, and a tap.
- 26. The coated member according to claim 1 wherein the outer region comprising a plurality of the coating sets wherein the thickness of each one of the coating sets is about equal.
- 27. The coated member according to claim 1 further including a finishing layer applied to the outer surface of the coating.
 - 28. The coated member according to claim 27 wherein the finishing layer comprising one or more layers of one or more of the following: alumina, and nitrides, aluminum nitrides and aluminum carbonitrides of one or more of titanium, niobium, hafnium, vanadium, tantalum, zirconium, chromium alone or in combination with each other or in combination with other metals.
 - 29. The coated member according to claim 27 further including a lubricous coating on the finishing coating.
 - 30. The coated member according to claim 1 wherein in the metal aluminum nitride nanolayer the aluminum/titanium atomic ratio ranges between about 0.2 to about 2.5.

- 31. The coated member according to claim 30 wherein the aluminum/titanium atomic ratio is greater than zero and less than 1.0.
- 32. The coated member according to claim 31 wherein the aluminum/titanium atomic ratio is greater than 0.2 and less than 0.9.
- 33. The coated member according to claim 30 wherein the aluminum/titanium atomic ratio is equal to or greater than 1.0 and less than 2.5.
- 34. The coated member according to claim 1 wherein the metal nitride nanolayer including aluminum therein, and the composition of the aluminum-containing metal nitride nanolayer being different from the composition of the metal aluminum nitride nanolayer.
- 35. The coated member according to claim 34 wherein the aluminum content in the aluminum-containing metal nitride nanolayer being less than the aluminum content in the metal aluminum nitride nanolayer.
- 36. The coated member according to claim 35 wherein the metal is titanium.
 - 37. A nanolayered coated member comprising:
- a substrate having a surface and a coating on the surface of the substrate;

the coating comprising a plurality of coating sets of nanolayers wherein each coating set comprising alternating nanolayers of a metal aluminum nitride and a metal aluminum carbonitride;

the coating including a bonding region and an outer region; and

the bonding region comprising a plurality of the coating sets wherein the thickness of each coating

set increases as one moves away from the surface of the substrate.

- 38. The coated member according to claim 37 wherein the metal is selected from the group comprising titanium, niobium, hafnium, vanadium, tantalum, molybdenum, zirconium, chromium and tungsten alone or in combination with each other or in combination with other metals.
- 39. The coated member according to claim 37 wherein the substrate is selected from the group comprising cemented carbide, cermet, ceramic, high speed steel, diamond, polycrystalline diamond, and polycrystalline cubic boron.
- wherein for each of the coating sets in the bonding region the thickness of the metal aluminum nitride nanolayer being different from the thickness of the metal aluminum carbonitride nanolayer.
 - 41. The coated member according to claim 37 wherein for each of the coating sets in the outer region the thickness of the metal aluminum nitride nanolayer being different than the thickness of the metal aluminum carbonitride nanolayer.
 - 42. The coated member according to claim 37 wherein the outer region comprising a plurality of the coating sets wherein the thickness of each coating set is about equal.
 - 43. The coated member according to claim 37 wherein the coated member comprising a cutting insert, the cutting insert having a rake surface and a flank

surface, the rake surface and the flank surface intersecting to form a cutting edge.

- 44. The coated member according to claim 37 wherein the metal is titanium, and for each of the coating sets the titanium aluminum nitride nanolayer having a thickness and the titanium aluminum carbonitride nanolayer having a thickness, and the thickness of the titanium aluminum nitride nanolayer being different from the thickness of the titanium aluminum carbonitride nanolayer.
- 45. The coated member according to claim 37 further including a finishing layer applied to the outer surface of the coating.
- wherein the finishing layer comprises one or more of the following: alumina, and nitrides, aluminum nitrides and aluminum carbonitrides of one or more of titanium, niobium, hafnium, vanadium, tantalum, zirconium, chromium alone or in combination with each other or in combination with other metals.
- 47. The coated member according to claim 37 further including a lubricious coating on the finishing coating.
- 48. The coated member according to claim 37 wherein in the metal aluminum nitride nanolayer the aluminum/titanium atomic ratio ranges between about 0.2 to about 2.5, and in the metal aluminum carbonitride nanolayer the aluminum/titanium atomic ratio ranges between about 0.2 and about 2.5.
- 49. The coated member according to claim 48 wherein the aluminum/titanium atomic ratio in the metal

aluminum nitride nanolayer is greater than zero and less than 1.0, and the aluminum/titanium atomic ratio in the metal aluminum carbonitride nanolayer is greater than zero and less than 1.0.

- 50. The coated member according to claim 49 wherein the aluminum/titanium atomic ratio in the metal aluminum nitride nanolayer is between 0.2 and 0.9, and the aluminum/titanium atomic ratio in the metal aluminum carbonitride nanolayer is between 0.2 and 0.9.
- 51. The coated member according to claim 37 wherein in the metal aluminum nitride nanolayer the aluminum/titanium atomic ratio ranges between greater than 1.0 and less than 2.5, and in the metal aluminum carbonitride nanolayer the aluminum/titanium atomic ratio ranges between greater than 1.0 and less than 2.5.
 - 52. A nanolayered coated member comprising:
 a substrate having a surface and a coating on
 the surface of the substrate;

the coating comprising a plurality of coating sets of nanolayers wherein each set comprising alternating nanolayers of a metal nitride and a metal aluminum nitride and a metal aluminum carbonitride;

the coating including a bonding region and an outer region; and

the bonding region comprising a plurality of the coating sets wherein the thickness of each coating set increases as one moves away from the surface of the substrate.

53. The coated member according to claim 52 wherein the metal is selected from the group comprising titanium, niobium, hafnium, vanadium, tantalum,

molybdenum, zirconium, chromium and tungsten alone or in combination with each other or in combination with other metals.

- 54. The coated member according to claim 52 wherein the substrate is selected from the group comprising cemented carbide, cermet, ceramic, high speed steel, diamond, polycrystalline diamond, and polycrystalline cubic boron nitride.
- wherein for each of the coating sets in the bonding region the thickness of the metal nitride nanolayer being different from the thickness of the metal aluminum nitride nanolayer, the thickness of the metal nitride nanolayer being different from the thickness of the metal nitride nanolayer being different from the thickness of the metal aluminum carbonitride nanolayer, and the thickness of the metal aluminum nitride nanolayer being different from the thickness of the metal aluminum carbonitride nanolayer.
- wherein for each of the coating sets in the outer region the thickness of the metal nitride nanolayer being different from the thickness of the metal aluminum nitride nanolayer, the thickness of the metal nitride nanolayer being different from the thickness of the metal nitride nanolayer being different from the thickness of the metal aluminum carbonitride nanolayer, and the thickness of the metal aluminum nitride nanolayer being different form the thickness of the metal aluminum carbonitride nanolayer.
- 57. The coated member according to claim 52 wherein the outer region comprising a plurality of the coating sets wherein the thickness of each coating set is about equal.

- 58. The coated member according to claim 52 wherein the coated member comprising one of the following: a cutting insert, an indexable cutting insert, a drill, a milling cutter, an end mill, a reamer and a tap.
- 59. The coated member according to claim 52 further including a finishing layer applied to the outer surface of the coating.
- wherein the finishing layer comprising one or more layers of one or more of the following: alumina, and nitrides, aluminum nitrides and aluminum carbonitrides of one or more of titanium, niobium, hafnium, vanadium, tantalum, zirconium, chromium alone or in combination with each other or in combination with other metals.
- 61. The coated member according to claim 59 further including a lubricious coating on the finishing coating.
- 62. The coated member according to claim 52 wherein in the metal aluminum nitride nanolayer the aluminum/titanium atomic ratio ranges between about 0.2 to about 2.5, and in the metal aluminum carbonitride nanolayer the aluminum/titanium atomic ratio ranges between about 0.2 and about 2.5.
- 63. The coated member according to claim 62 wherein the aluminum/titanium atomic ratio in the metal aluminum nitride nanolayer is greater than zero and less than 1.0, and the aluminum/titanium atomic ratio in the metal aluminum carbonitride nanolayer is greater than zero and less than 1.0.

- 64. The coated member according to claim 63 wherein the aluminum/titanium atomic ratio in the metal aluminum nitride nanolayer is between 0.2 and 0.9, and the aluminum/titanium atomic ratio in the metal aluminum carbonitride nanolayer is between 0.2 and 0.9.
- 65. The coated member according to claim 52 wherein in the metal aluminum nitride nanolayer the aluminum/titanium atomic ratio ranges between greater than 1.0 and less than 2.5, and in the metal aluminum carbonitride nanolayer the aluminum/titanium atomic ratio ranges between greater than 1.0 and less than 2.5.
- 66. The coated member according to claim 52 wherein the metal nitride nanolayer including aluminum therein, and the composition of the aluminum-containing metal nitride nanolayer being different from the composition of the metal aluminum nitride nanolayer.
- 67. The coated member according to claim 66 wherein the aluminum content in the aluminum-containing metal nitride nanolayer is less than the aluminum content in the metal aluminum nitride nanolayer.
- 68. The coated member according to claim 67 wherein the metal is titanium.
- 69. A process for making a nanolayered coated member, the process comprising the steps of:
 providing a substrate having a surface;
 providing a metal target;
 providing a metal aluminum target;
 rotating a substrate between the metal target and the metal aluminum target;

supplying electrical power at a first level to the metal target;

supplying electrical power at the first level to the metal aluminum target;

depositing a coating comprising coating sets of alternating nanolayers on the surface of the substrate;

changing the deposition rate of the alternating nanolayers over a selected period of time during which electrical power supplied to the metal target and the metal-aluminum target changes from the first level to a second level; and

controlling the deposition rate of the alternating nanolayers for a period of time after the electrical power reaches the second level.

- 70. The process according to claim 69 wherein the alternating nanolayers comprise a metal nitride and a metal aluminum nitride.
 - 71. The process according to claim 69 wherein the alternating nanolayers comprise a metal nitride and a metal aluminum nitride, the depositing step includes depositing a plurality of coating sets of the alternating nanolayers during the time the electric power to the metal target and to the metal aluminum target changes from the first to the second level so as to deposit a bonding region of the coating.
 - 72. The process according to claim 71 wherein each coating set included in the bonding region has a thickness, and the thickness of the coating sets in the bonding region increases as one moves away from the surface of the substrate.

- 73. The process according to claim 69 the depositing step includes depositing a plurality of the coating sets of the alternating nanolayers during the time after the electrical power has reached the second level so as to deposit an outer region of the coating.
- 74. The process according to claim 73 wherein each coating set included in the outer region has a thickness, and the thickness of each one of the coating sets remaining about equal.
- wherein for the outer region the metal nitride
 nanolayer has a thickness and the metal aluminum
 nitride nanolayer has a thickness, and the thickness of
 the metal aluminum nitride nanolayer being different
 from the thickness of the metal nitride nanolayer.
- 76. The process according to claim 70 wherein for the bonding region the metal nitride nanolayer has a thickness and the metal aluminum nitride nanolayer has a thickness, and the thickness of the metal aluminum nitride nanolayer being different from the thickness of the metal nitride nanolayer.
- 77. The process according to claim 69 further including depositing a finishing layer on the outer surface of the coating.
- 78. The process according to claim 77 wherein the finishing layer comprising one or more layers of one or more of the following: alumina, and nitrides, aluminum nitrides and aluminum carbonitrides of one or more of titanium, niobium, hafnium, vanadium, tantalum, zirconium, chromium alone or in combination with each other or in combination with other metals.

- 79. The process according to claim 77 further including depositing a lubricious layer on the surface of the finishing layer.
- 80. The process according to claim 69 wherein the coated member comprising one of the following: a cutting insert, an indexable cutting insert, a drill, a milling cutter, an end mill, a reamer and a tap.
- 81. The process according to claim 69 further including supplying nitrogen at a pre-selected nitrogen partial flow rate.
- 82. The process according to claim 81 wherein the nitrogen partial flow rate is below 0.5.
- 83. The process according to claim 81 wherein the nitrogen partial flow rate is below 0.4.
- 84. The process according to claim 81 wherein the nitrogen partial flow rate ranges between about 0.35 and about 0.2.
- 85. The process according to claim 69 wherein the first level of electrical power is less than the second level of electrical power.
- 86. A process for making a nanolayered coated member, the process comprising the steps of: providing a substrate having a surface;

providing a metal-aluminum target;

providing a metal-aluminum-carbon target;

rotating a substrate between the metalaluminum target and the metal-aluminum-carbon target;

supplying electrical power at a first level
to the metal-aluminum target;

supplying electrical power at the first level to the metal-aluminum-carbon target;

depositing a coating comprising coating sets of alternating nanolayers on the surface of the substrate:

changing the deposition rate of the alternating nanolayers over a selected period of time during which electrical power supplied to the metal-aluminum target and to the metal-aluminum-carbon target changes from the first level to a second level; and

controlling the deposition rate of the alternating nanolayers for a period of time after the electrical power reaches the second level.

- 87. The process according to claim 86 wherein the depositing step comprises depositing a plurality of coating sets of alternating nanolayers of metal aluminum nitride and a metal aluminum carbonitride.
- 88. The process according to claim 86 wherein the depositing step includes depositing a plurality of coating sets of alternating nanolayers of metal aluminum nitride and metal aluminum carbonitride during the time the electric power is increased to the metal-aluminum target and to the metal-aluminum-carbon target so as to deposit a bonding region of the coating.
- 89. The process according to claim 88 wherein each one of the coating sets included in the bonding region has a thickness and the thickness of the coating sets increases as one moves away from the surface of the substrate.

- 90. The process according to claim 88 wherein the depositing step further includes depositing a plurality of alternating nanolayers of metal aluminum nitride and metal aluminum carbonitride during the time after the electrical power has reached the second level as to deposit an outer region of the coating.
- 91. The process according to claim 90 wherein each one of the coating sets included in the outer region has a thickness, and the thickness of the coating sets remaining about equal.
- 92. The process according to claim 86 wherein the depositing step comprises depositing a plurality of coating sets of alternating layers of metal aluminum nitride and metal aluminum carbonitride so as to form a bonding region:
 - wherein for the bonding region the metal aluminum nitride layer has a thickness and the metal aluminum carbonitride layer has a thickness, and the thickness of the metal aluminum carbonitride layer being different from the thickness of the metal aluminum nitride layer.
- 94. The process according to claim 86 wherein the depositing step comprises depositing a plurality of coating sets of alternating layers of metal aluminum nitride and metal aluminum carbonitride so as to form an outer region.
- 95. The process according to claim 94 wherein for the outer region the metal aluminum nitride layer has a thickness and the metal aluminum carbonitride layer has a thickness, and the thickness

of the metal aluminum carbonitride layer being different from the thickness of the metal aluminum nitride layer.

- 96. The process according to claim 86 further including depositing a finishing layer on the outer surface of the coating.
- 97. The process according to claim 96 wherein the finishing layer comprising one or more layers of one or more of the following: alumina, and nitrides, aluminum nitrides and aluminum carbonitrides of one or more of titanium, niobium, hafnium, vanadium, tantalum, zirconium, chromium alone or in combination with each other or in combination with other metals.
- 98. The process according to claim 96 further including depositing a lubricious coating on the surface of the finishing coating.
- 99. The process according to claim 86 wherein the coated member comprising a cutting insert, a drill, an end mill, a milling cutter, a reamer and a tap.
- 100. The process according to claim 86 further including supplying nitrogen at a pre-selected nitrogen partial flow rate.
- 101. The process according to claim 100 wherein the nitrogen partial flow rate is below 0.5.
- 102. The process according to claim 100 wherein the nitrogen partial flow rate is below 0.4.
- 103. The process according to claim 100 wherein the nitrogen partial flow rate ranges between about 0.35 and about 0.2.

104. The process according to claim 86 wherein the first level of electrical power is less than the second level of electrical power.

105. A process for making a nanolayered coated member, the process comprising the steps of:

providing a substrate having a surface;

providing a metal target;

providing a metal aluminum target;

providing a metal-aluminum-carbon target;

rotating a substrate between the metal target and the metal aluminum target and the metal-aluminum-carbon;

supplying electrical power at a first level to the metal target;

supplying electrical power at the first level to the metal aluminum target;

supplying electrical power at the first level to the metal-aluminum-carbon target;

depositing a coating comprising coating sets of alternating nanolayers on the surface of the substrate;

changing the deposition rate of the alternating nanolayers over a selected period of time during which electrical power supplied to the metal target and to the metal-aluminum target and to the metal-aluminum-carbon target changes from the first level to a second level; and

controlling the deposition rate of the alternating nanolayers for a period of time after the electrical power reaches the second level.

106. The process according to claim 105 wherein the depositing step comprises depositing a plurality of coating sets of alternating nanolayers of

a metal nitride and a metal aluminum nitride and a metal aluminum carbonitride.

- wherein the depositing step includes depositing a plurality of coating sets of alternating nanolayers of metal nitride and metal aluminum nitride and a metal aluminum carbonitride during the time the electric power is increased to the metal target and the metal aluminum target and the metal aluminum carbon target so as to deposit a bonding region.
- wherein for the bonding region each coating set included in the bonding region has a thickness and the thickness of each coating set increases as one moves away from the surface of the substrate.
- wherein the depositing step further includes depositing a plurality of alternating nanolayers of metal nitride and metal aluminum nitride and metal aluminum carbonitride during the time after the electrical power has reached the second level so as to deposit an outer region.
- 110. The process according to claim 109 wherein for the outer region each coating set included in the outer region has a thickness, and the thickness of each one of the coating sets remaining about equal.
- 111. The process according to claim 105 wherein the depositing step comprises depositing a plurality of coating sets of alternating layers of metal nitride and metal aluminum nitride and metal aluminum carbonitride so as to form a bonding region.

- wherein for each of the coating sets in the bonding region the metal nitride nanolayer has a thickness and the metal aluminum nitride nanolayer has a thickness and the metal aluminum carbonitride nanolayer has a thickness, and the thickness of the metal aluminum nitride layer being different from the thickness of the metal nitride nanolayer and the thickness of the metal aluminum nitride nanolayer being different from the thickness of the metal aluminum nitride nanolayer being different from the thickness of the metal aluminum carbonitride nanolayer, and the thickness of the metal aluminum nitride nanolayer being different from the thickness of the metal aluminum nitride nanolayer being different from the thickness of the metal aluminum carbonitride nanolayer.
- 113. The process according to claim 105 wherein the depositing step comprises depositing a plurality of coating sets of alternating layers of metal nitride and metal aluminum nitride and metal aluminum carbonitride so as to form an outer region.
 - wherein for each of the coating sets in the outer region the metal nitride layer has a thickness and the metal aluminum nitride layer has a thickness and the metal aluminum carbonitride layer has a thickness, and the thickness of the metal aluminum nitride layer being different from the thickness of the metal nitride layer and the thickness of the metal aluminum carbonitride layer, and the thickness of the metal aluminum nitride layer, and the thickness of the metal aluminum nitride layer being different from the thickness of the metal aluminum nitride layer being different from the thickness of the metal aluminum carbonitride layer.
 - 115. The process according to claim 105 further including a depositing a finishing layer on the outer surface of the coating.

- wherein the finishing layer comprising one or more layers of one or more of the following: alumina and nitrides, aluminum nitrides and aluminum carbonitrides of one or more of titanium, niobium, hafnium, vanadium, tantalum, zirconium, chromium alone or in combination with each other or in combination with other metals.
- 117. The process according to claim 115 further including depositing a lubricious coating on the surface of the finishing coating.
- 118. The process according to claim 105 wherein the coated member comprising a cutting insert, a drill, a milling cutter, an end mill, a reamer and a tap.
- 119. The process according to claim 105 further including supplying nitrogen at a pre-selected nitrogen partial flow rate.
- 120. The process according to claim 119 wherein the nitrogen partial flow rate is below 0.5.
- 121. The process according to claim 119 wherein the nitrogen partial flow rate is below 0.4.
- 122. The process according to claim 119 wherein the nitrogen partial flow rate ranges between about 0.35 and about 0.2.
- 123. The process according to claim 105 wherein the first level of electrical power is less than the second level of electrical power.

the coating comprising a plurality of coating sets of nanolayers wherein each coating set comprising alternating nanolayers of titanium aluminum nitride and titanium aluminum carbonitride.

- 125. The nanolayered coated member according to claim 124 wherein the coating including a bonding region, the bonding region being adjacent to the substrate surface.
- 126. The nanolayered coated member according to claim 125 wherein the bonding region comprising a plurality of the coating sets wherein the thickness of each coating set increases as one moves away from the surface of the substrate.
- 127. The nanolayered coated member according to claim 125 wherein the coating including an outer region, the outer region being adjacent to the bonding region.
- 128. The nanolayered coated member according to claim 125 wherein the outer region comprising a plurality of the coating sets, and wherein the thickness of each one of the coating set being about equal.

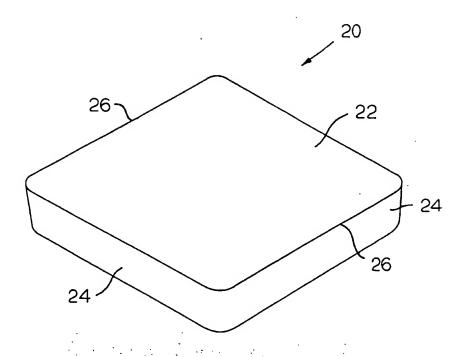


FIG. I

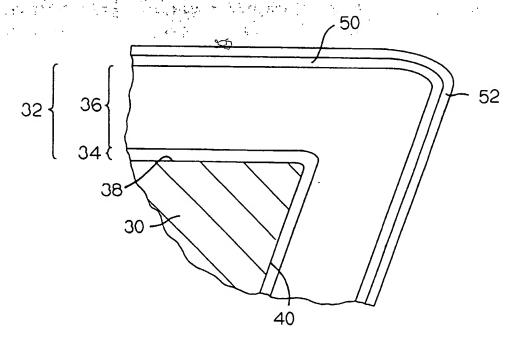


FIG. 2

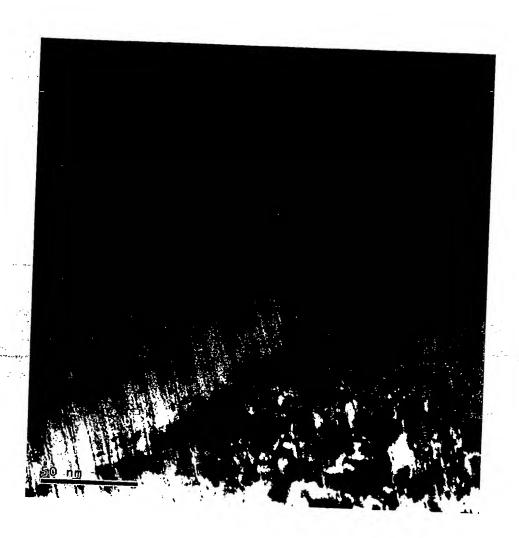


FIG. 3



FIG. 4



FIG. 5

'INTERNATIONAL SEARCH REPORT

Internation Application No

PCT/US 03/06953 A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C23C30/00 C23C C23C28/04 C23C14/02 According to International Patent Classification (IPC) or to both national classification and IPC B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 C23C Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, COMPENDEX, WPI Data, PAJ C. DOCUMENTS CONSIDERED TO BE RELEVANT Category * Citation of document, with indication, where appropriate, of the relevant passages Relevant to daim No. X EP 0 701 982 A (SUMITOMO ELECTRIC 1-128 INDUSTRIES) 20 March 1996 (1996-03-20) page 2, line 54 -page 4, line 38; claims; figures 1-6; table 2 US 6 103 357 A (STRONDL CHRISTIAN ET AL) 1 - 36, X 15 August 2000 (2000-08-15) 69-85 cited in the application í column 3, line 66 -column 4, line 12; claims; examples Patent family members are listed in annex. Further documents are listed in the continuation of box C. Special categories of cited documents: "T" later document published after the international filing date or priority date and not in conflict with the application but clied to understand the principle or theory underlying the *A* document defining the general state of the art which is not considered to be of particular relevance Invention *E* earlier document but published on or after the international "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention citation or other special reason (as specified) cannot be considered to involve an inventive step when the document is combined with one or more other such docu-*O* document referring to an oral disclosure, use, exhibition or ments, such combination being obvious to a person skilled in the art. other means *P* document published prior to the international filing date but later than the priority date claimed "&" document member of the same patent family Date of the actual completion of the international search Date of mailing of the international search report 10 July 2003 04/08/2003 Name and mailing address of the ISA Authorized officer

European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016

Mauger, J

INTERNATIONAL SEARCH REPORT

Internat Application No PCT/US 03/06953

C.(Continu	etion) DOCUMENTS CONSIDERED TO BE RELEVANT	PCT/US 03/06953
Category *	Citation of document, with indication, where appropriate, of the relevant passages	
x		Relevant to claim No.
	ANDERSEN K N ET AL: "Deposition, microstructure and mechanical and tribological properties of magnetron sputtered Tin/TiAlN multilayers" SURF COAT TECHNOL; SURFACE AND COATINGS TECHNOLOGY 2000 ELSEVIER SEQUOIA SA, LAUSANNE, SWITZERLAND, vol. 123, no. 2, 2000, pages 219-226, XP002247207 cited in the application "2. Experimental", "3.2 mechanical properties", "3.3 tribological properties" figures 5,7	1-36, 69-85
A	KAWATA K ET AL: "Characterization of multilayer films of Ti-Al-O-C-N system prepared by pulsed d.c. plasma-enhanced chemical vapor deposition" THIN SOLID FILMS, ELSEVIER-SEQUOIA S.A. LAUSANNE, CH, vol. 390, no. 1-2, 30 June 2001 (2001-06-30), pages 64-69, XP004246650 ISSN: 0040-6090	1-128
	the whole document	
	,	

'INTERNATIONAL SEARCH REPORT

Innumation on patent family members

Internation Application No
PCT/US 03/06953

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
EP 0701982	A	20-03-1996	DE DE EP JP US	69527236 D1 69527236 T2 0701982 A1 8134629 A 5700551 A	08-08-2002 20-03-2003 20-03-1996 28-05-1996 23-12-1997
US 6103357	A	15-08-2000	SE EP JP SE WO	518145 C2 0983393 A1 2001521447 T 9701494 A 9848072 A1	03-09-2002 08-03-2000 06-11-2001 19-02-1999 29-10-1998

THIS PAGE BLANK (USPTO)

This Page is Inserted by IFW Indexing and Scanning Operations and is not part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

BLACK BORDERS

IMAGE CUT OFF AT TOP, BOTTOM OR SIDES

FADED TEXT OR DRAWING

BLURRED OR ILLEGIBLE TEXT OR DRAWING

SKEWED/SLANTED IMAGES

COLOR OR BLACK AND WHITE PHOTOGRAPHS

GRAY SCALE DOCUMENTS

LINES OR MARKS ON ORIGINAL DOCUMENT

REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY

IMAGES ARE BEST AVAILABLE COPY.

☐ OTHER:

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

THIS PAGE BLANK (USPTO)